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Use of Markov Chains in Treating Depropagation in Copolymerization. I. Composition of Copolymers

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ABSTRACT

Equations for the composition of the copolymers in binary, ternary, and K-component copolymerization with depropagation developed by means of Markov chains. The mole fractions of the different monomers in the copolymers are determined as components of the limit vector $\bar{a} = (a_1, \dots, a_n)$, the latter being obtained as an eigenvector of the transition matrix P. The elements of this matrix are so defined that they reflect the possibility of slipping one, two, or K types of monomer units off the growing chain in the K-component copolymerization ($K = 2, 3, \dots, n$). We take the case in which the monomer units slip off if they are attached to a chain, ending with one or more monomer units of the same type. Calculated and experimental data for the composition of the copolymers of α -methylstyrene and methyl methacrylate obtained by radical copolymerization are given. These data agree very well. It is shown that after small simplifications, the equations

developed can also be used for common copolymerization (without depropagation).

INTRODUCTION

In the polymerization of monomers with low heat of polymerization (α -methylstyrene, acetone, aldehydes) having low ceiling temperatures, depropagation is significant, even at normal temperature. The first theoretical study of the binary copolymerization with depropagation was made by Lowry [1]. Ivin and O'Driscoll [2-5] showed that experimental results of the copolymerization of α -methylstyrene with other monomers can be described by the equation given by Lowry. Later Wittmer [6] analyzed and developed in more detail one of the variants in Lowry's model. In this work are given experimental results of the copolymerization of α -methylstyrene and methyl methacrylate, described by the theoretical equations. Fisher [7] used Wittmer's equations to treat the experimental results of the copolymerization of α -methylstyrene and styrene. Inaki [8] by means of Lowry's model recognized the influence of depropagation in the cationic polymerization of these monomers.

Price [9] was the one to use Markov chains to describe the composition and the tacticity of the copolymers. Subsequently, this method was used in the physical chemistry of polymers to optimize the properties and the processes for polymer preparation [10, 11]. However, simulation of copolymerization with depropagation by means of Markov chains has not been studied yet. In the present work the method of finite Markov chains is used for this purpose [12]. This enables us to develop equations for the composition of the copolymers in the binary, ternary, and K-component copolymerization, where depropagation at one, two, or K monomer units from the growing chain is possible.

RESULTS AND DISCUSSION

Binary Copolymerization

Let the polymerization be carried out at a temperature near the ceiling temperature of the monomer M_1 . Then it can be supposed that: (a) M_2 does not depropagate; (b) M_1 depropagates if the monomer unit m_1 is attached to the growing chains ending with the same monomer unit and does not depropagate in other cases.

$$\mu = \frac{[\sim (m_1)_{n+1}^*]}{[\sim (m_1)_n^*]} \quad 1 \leq n < \infty \quad (4)$$

and the equilibrium constant K is taken into consideration:

$$K = k_{11}^{pol.} / k_{11}^{dep.} \quad (5)$$

then:

$$P_{12} = \frac{k_{12} \sum_{n=1}^{\infty} [\sim (m_1)_1^*] [M_1]}{k_{11}^{pol.} \sum_{n=1}^{\infty} [(m_1)_n^*] [M_1] + k_{11}^{dep.} \sum_{n=2}^{\infty} [(m_1)_n^*] + k_{12} \sum_{n=1}^{\infty} [(m_1)_1^*] [M_2]} \cdot \frac{[M_2] \cdot r_1^{-1}}{[M_1] + \mu K^{-1} + [M_2] r_1^{-1}} \quad (6)$$

Solving the right-hand side of Eq. (6) yields

$$\frac{\sum_{n=2}^{\infty} [(m_1)_n^*]}{\sum_{n=1}^{\infty} [(m_1)_n^*]} = 1 - \frac{[(m_1)_1^*]}{\sum_{n=1}^{\infty} [(m_1)_n^*]} \quad (7)$$

By means of Eq. (4) it is found that:

$$\frac{[(m_1)_1^*]}{\sum_{n=1}^{\infty} [(m_1)_n^*]} = 1 - \mu \quad (8)$$

Consequently:

$$\frac{\sum_{n=2}^{\infty} [(m_1)_n^*]}{\sum_{n=1}^{\infty} [(m_1)_n^*]} = \mu \quad (9)$$

To express μ by experimentally definable quantities, the stationality equation for active particles of the type $\sim (m_1)_2^*$ can be used:

$$k_{11}^{\text{pol.}} [(m_1)_1^*] [M_1] + k_{11}^{\text{dep.}} [(m_1)_3^*] - k_{11}^{\text{pol.}} [(m_1)_2^*] [M_1] - k_{12} [(m_1)_2^*] - k_{11}^{\text{dep.}} [(m_1)_2^*] = 0 \quad (10)$$

After dividing this equation by $k_{11}^{\text{pol.}} [(m_1)_1^*]$ and solving the quadratic equation obtained the experimentally definable quantities are expressed by Eq. (11):

$$\mu = \frac{[M_2] r_1^{-1} + [M_1] + K^{-1} - \{([M_2] r_1^{-1} + [M_1] + K^{-1})^2 - 4K^{-1}[M_1]\}^{0.5}}{2K^{-1}} \quad (11)$$

The symbol μ is so chosen that $\mu \rightarrow 0$ when $[M_1] \rightarrow 0$, and $\mu \rightarrow 1$ when $[M_2] \rightarrow 0$.

The limit vector $\bar{a} = (a_1, a_2)$ (i.e., the limit matrix A , the two rows of which are equal to \bar{a}) is determined as the eigenvector of the matrix P [12] and in this case is equal to:

$$\bar{a} = \left(\frac{P_{21}}{P_{12} + P_{21}}, \frac{P_{12}}{P_{12} + P_{21}} \right) \quad (12)$$

The components a_1 and a_2 represent the probabilities of the foundation of the growing chain in conditions M_1 and M_2 , respectively. These components a_1 and a_2 also indicate the portion of monomer units m_1 and m_2 , respectively, in the macromolecules in a large number of steps in growth of the latter. Consequently:

$$\frac{[m_1]}{[m_2]} = \frac{a_1}{a_2} = \frac{P_{21}}{P_{12}} = \frac{[M_1] r_2^{-1} \{ [M_1] + [M_2] r_1^{-1} + \mu K \}}{[M_2] r_1^{-1} \{ [M_1] r_2 + [M_2] \}} \quad (13)$$

If the equilibrium constant K is determined by independent experiment it is possible to predict the composition of the copolymer by using Eq. (13) when r_1 and r_2 are known and, conversely, knowing the composition, to determine r_1 and r_2 .

Further information for the copolymers is obtained by means of the fundamental matrix Z of the examined Markov chain [12]

$$Z = \begin{pmatrix} P_{21} + \frac{P_{12}}{P_{12} + P_{21}} & P_{12} - \frac{P_{12}}{P_{12} + P_{21}} \\ P_{21} - \frac{P_{21}}{P_{12} + P_{21}} & P_{12} + \frac{P_{21}}{P_{12} + P_{21}} \end{pmatrix} \quad (14)$$

The elements of the matrix Z allow one to determine more exactly the composition of the copolymer in the case when the average degree of polymerization \bar{N} is known.

From Kemeny and Snell [12] it follows that, for finite \bar{N} , the average number of units of the type m_j in the macromolecules which begin its building with a unit m_i [$M_i(m_j)$] will differ from the calculated ($\bar{N}a_j$) based on the limit probabilities of the quantity

$$M_i(m_j) - \bar{N}a_j \approx Z_{ij} - a_j \quad (15)$$

In the case examined, for example,

$$M_1(m_2) - \bar{N}a_2 \approx \frac{P_{12}}{(P_{12} + P_{21})^2} \quad (16)$$

In addition, the matrix Z allows the matrix of the covariations C to be determined [12]. The diagonal elements of this matrix are in reality components of the vector of the limit dispersions: $\bar{\beta} = (B_1, B_2)$. These are really dispersions of the random variable, expressing the

content of the different monomer units in the copolymer. In the examined case the matrix of covariations is equal to:

$$C = \frac{P_{12}P_{21}(2 - P_{12} - P_{21})}{(P_{12} + P_{21})^3} \cdot \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \quad (17)$$

Consequently, $B_1 = B_2$.

These regularities are used for treatment of the results of the copolymerization of α -methylstyrene (M_1) and methyl methacrylate (M_2) at the ceiling temperature of M_1 (60° C). The copolymerization constants (r_1 and r_2), the equilibrium constant K , and the experimental results for the composition of the copolymers are taken from Wittmer [6]. In Table 1 are shown the results of the calculations for the parameter μ made from Eq. (13), the transition probabilities P_{12} and P_{21} calculated by Eqs. (6) and (3), the mole fractions of the monomer units in the copolymers based on Eq. (13) and their dispersions (b_i).

TABLE 1. Comparison between Experimental [6] and the Calculated Compositions of the Copolymers of α -Methylstyrene (M_1) and Methyl Methacrylate (M_2)^a

No.	Monomer M_1 (mole fraction)	μ	P_{12}	P_{21}	Mole fraction of M_1 in the copolymer		$b_1 = b_2$
					Calcd	Exptl	
1	0.06	0.02	0.98	0.10	0.096	0.096	0.083
2	0.10	0.03	0.97	0.17	0.148	0.177	0.109
3	0.20	0.07	0.93	0.31	0.251	0.254	0.143
4	0.30	0.11	0.87	0.44	0.335	0.335	0.155
5	0.40	0.16	0.83	0.55	0.398	0.397	0.149
6	0.50	0.22	0.76	0.65	0.451	0.447	0.147
7	0.60	0.30	0.68	0.73	0.518	0.520	0.147
8	0.70	0.40	0.58	0.82	0.586	0.587	0.143
9	0.80	0.53	0.44	0.88	0.665	0.660	0.151

^a Conditions: $T = 60^\circ \text{C}$; $r_1 = 0.30$, $r_2 = 0.55$; $K = 0.14$ liter/mole [6].

It is seen from Table 1 that the experimental and the calculated compositions of the copolymers correlate very well. The quantities b_1 and b_2 are the dispersions of the mole fractions of the monomer units in the copolymers.

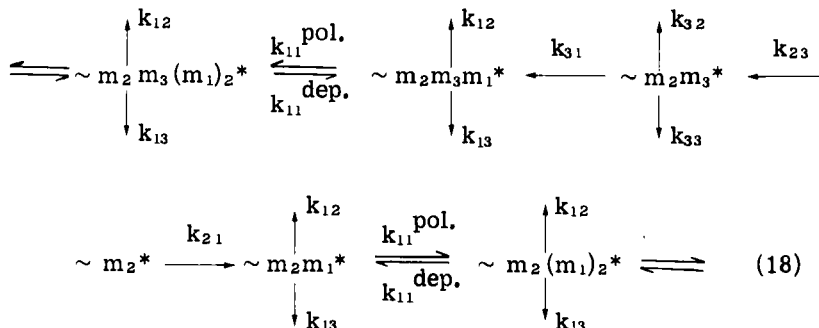
If the second monomer M_2 also depropagates, then the equations for the composition of the copolymer remain in the same form. Only the expressions for the transition probabilities P_{21} and P_{22} change. Such a situation will be further discussed in the next part of the present work.

Ternary Copolymerization

Ternary Copolymerization of Monomers Where Only One Monomer Depolymerizes

The initial suppositions are: M_1 is able to depolymerize when it attaches to a growing chain of the type $\sim m_1^*$ and does not depolymerize in other cases; M_2 and M_3 do not depolymerize.

The copolymerization can be expressed by the scheme (18).



The growing macromolecule also can be compared with a regular Markov chain with three positions M_1 , M_2 , and M_3 , which correspond to the three types of active ends:

The transitional probabilities P_{ij} ($2 \leq i \leq 3$, $1 \leq j \leq 3$) can be expressed in the following way as seen in scheme (18)

$$P_{ij} = \frac{[M_j] r_{ij}^{-1}}{\sum_{j=1}^3 [M_j] r_{ij}^{-1}} \quad (19)$$

if we accept that $r_{ii} = 1$. Determination of P_{11} , P_{12} , and P_{13} proceeds in the same way as determination of P_{11} and P_{12} in the previous section. If the parameter μ_1 which is expressed by Eqs. (4) and (11) and also the equilibrium polymerization-depolymerization constant K_1 expressed by Eq. (5) are introduced, then:

$$P_{11} = \frac{[M_1] + \mu_1 K_1^{-1}}{[M_1] + \mu_1 K_1^{-1} + [M_2] r_{12}^{-1} + [M_3] r_{13}^{-1}} \quad (20)$$

$$P_{1k} = \frac{[M_k] r_{1k}^{-1}}{[M_1] + \mu_1 K_1^{-1} + [M_2] r_{12}^{-1} + [M_3] r_{13}^{-1}}; \quad K = 2, 3 \quad (21)$$

As mentioned earlier, μ_1 can be expressed by experimentally definable quantities:

$$\mu_1 =$$

$$\frac{[M_1] + [M_2]r_{12}^{-1} + [M_3]r_{13}^{-1} + K_1^{-1} - \{([M_1] + [M_2]r_{12}^{-1} + [M_3]r_{13}^{-1} + K_1^{-1})^2 - 4[M_1]K_1^{-1}\}^{0.5}}{2K_1^{-1}} \quad (22)$$

The components of the limit vector $\bar{a} = (a_1, a_2, a_3)$ in this case are:

$$a_1 = \frac{1}{A} \{ P_{11} + P_{12}(P_{33} - P_{23}) + P_{13}(P_{22} - P_{32}) \} \quad (23)$$

$$a_2 = \frac{1}{A} \{ P_{12}(1 + P_{13} - P_{33}) - P_{13}(P_{12} - P_{32}) \} \quad (24)$$

$$a_3 = \frac{1}{A} \{ P_{13}(1 + P_{12} - P_{22}) - P_{12}(P_{13} - P_{23}) \} \quad (25)$$

where:

$$A = \begin{vmatrix} 1 + P_{12} - P_{22} & P_{12} - P_{32} \\ P_{13} - P_{23} & 1 + P_{13} - P_{33} \end{vmatrix} \quad (26)$$

Then the composition of the copolymer can be expressed by the ratios

$$\frac{[m_1]}{[m_2]} = \frac{a_1}{a_2} =$$

$$\frac{[M_1] \left(\sum_{j=1}^3 f_1^j + \frac{\mu_1}{K_1} \right)^{-1} + \frac{f_1^2 \left(\sum_{j=1}^3 f_1^j \right)^{-1}}{\left\{ [M_3] \left(\sum_{j=1}^3 f_3^j \right)^{-1} - f_2^3 \left(\sum_{j=1}^3 f_2^j \right)^{-1} \right\}^{-1}} + \frac{f_1^3 \left(\sum_{j=1}^3 f_1^j \right)^{-1}}{\left\{ [M_2] \left(\sum_{j=1}^3 f_2^j \right)^{-1} - f_3^2 \left(\sum_{j=1}^3 f_3^j \right)^{-1} \right\}^{-1}}}{\frac{f_1^2 \left(\sum_{j=1}^3 f_1^j \right)^{-1}}{\left\{ 1 + f_1^3 \left(\sum_{j=1}^3 f_1^j \right)^{-1} - [M_3] \left(\sum_{j=1}^3 f_3^j \right)^{-1} \right\}^{-1}} - \frac{f_1^3 \left(\sum_{j=1}^3 f_3^j \right)^{-1}}{\left\{ f_1^2 \left(\sum_{j=1}^3 f_1^j \right)^{-1} - f_3^2 \left(\sum_{j=1}^3 P_3^j \right)^{-1} \right\}^{-1}}} \quad (27)$$

$$\frac{[m_2]}{[m_3]} = \frac{a_2}{a_3} =$$

$$\frac{\frac{f_1^2 \left(\sum_{j=1}^3 f_1^j \right)^{-1}}{\left\{ 1 + f_1^3 \left(\sum_{j=1}^3 f_1^j \right)^{-1} - [M_3] \left(\sum_{j=1}^3 f_3^j \right)^{-1} \right\}^{-1}} - \frac{f_1^3 \left(\sum_{j=1}^3 f_1^j \right)^{-1}}{f_1^2 \left(\sum_{j=1}^3 f_1^j \right)^{-1}}}{\frac{f_1^3 \left(\sum_{j=1}^3 f_1^j \right)^{-1}}{\left\{ 1 + f_1^2 \left(\sum_{j=1}^3 f_1^j \right)^{-1} - [M_2] \left(\sum_{j=1}^3 f_2^j \right)^{-1} \right\}^{-1}} - \frac{f_1^3 \left(\sum_{j=1}^3 f_1^j \right)^{-1}}{f_2^3 \left(\sum_{j=1}^3 f_2^j \right)^{-1}}}$$

(28)

where

$$f_i^j = \frac{[M_j]}{r_{ij}} \quad (29)$$

The ratio $[m_1]:[m_3] = a_1:a_3$ is obtained from Eqs. (27) and (28). These ratios as well as Eq. (22) in an independent determination of the equilibrium constant K_1 fully describe the composition of the obtained copolymers. The constants of copolymerization can be determined from the binary copolymerization of the possible monomer pairs when equations from the previous section are used.

The fundamental matrix Z in this case is:

$$Z = \frac{1}{B} \begin{pmatrix} A_{11} & A_{21} & A_{31} \\ A_{12} & A_{22} & A_{32} \\ A_{13} & A_{23} & A_{33} \end{pmatrix} \quad (30)$$

where A_{ij} and B are, respectively, the cofactors and the determinant of the matrix:

$$I - (P - A) = \begin{pmatrix} 1 + a_1 - P_{11} & a_2 - P_{12} & a_3 - P_{13} \\ a_1 - P_{21} & 1 + a_2 - P_{22} & a_3 - P_{23} \\ a_1 - P_{31} & a_2 - P_{32} & 1 + a_3 - P_{33} \end{pmatrix} \quad (31)$$

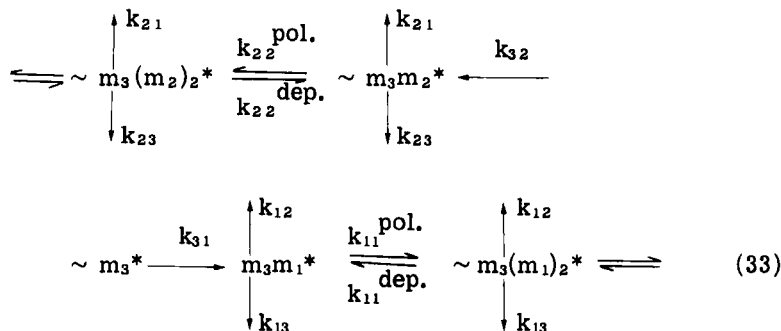
The diagonal elements of covariation matrix C , i.e., the components of the vector of the limit dispersions $\bar{\beta} = (B_1, B_2, B_3)$ are equal to:

$$\bar{\beta} = \{a_1(2Z_{11} - 1 - a_1), a_2(2Z_{22} - 1 - a_2), a_3(2Z_{33} - 1 - a_3)\} \quad (32)$$

Ternary Copolymerization of Monomers of Which Two Are Able to Depolymerize

The initial suppositions are: M_1 and M_2 depolymerize if attached respectively to the chains $\sim m_1^*$ and $\sim m_2^*$ and do not depolymerize otherwise; M_3 does not depolymerize.

In this case copolymerization can be expressed as shown in the scheme (33).



It is necessary to determine the equilibrium constants $K_1 = k_{11}^{\text{pol.}} (k_{11}^{\text{dep.}})^{-1}$ and $K_2 = k_{22}^{\text{pol.}} (k_{22}^{\text{dep.}})^{-1}$ by means of an independent experiment. If

$$\mu_i = \frac{[(m_i)_{n+1}]}{[(m_i)_n^*]} \quad i = 1, 2 \quad (34)$$

then the transition probabilities P_{i1} , P_{i2} , and P_{i3} ($i = 1, 2$) are:

$$P_{ii} = \frac{[M_i] + \mu_i K_i^{-1}}{[M_i] + \mu_i K_i^{-1} + \sum_{k=1; k \neq i}^3 [M_k] r_{ik}^{-1}} \quad i = 1, 2 \quad (35)$$

$$P_{ij} = \frac{[M_i] r_{ij}^{-1}}{[M_i] + \mu_i K_i^{-1} + \sum_{k=1; k \neq i}^3 [M_k] r_{jk}^{-1}} \quad i = 1, 2; 1 \leq j \leq 3 \quad (36)$$

The other transition probabilities P_{31} , P_{32} and P_{33} are based on Eq. (19).

To express μ_1 and μ_2 by experimentally definable quantities the respective stationary equations for $[\sim (m_1)_2^*]$ and $[\sim (m_2)_2^*]$ can be used. The expression (37) for μ_i is obtained.

$$\mu_i = \frac{[M_i] + \sum_{j=1; j \neq i}^3 [M_j] r_{ij}^{-1} + K_i^{-1} - \{([M_i] + \sum_{j=1; j \neq i}^3 [M_j] r_{ij}^{-1} + K_i^{-1})^2 - 4[M_i]K_i^{-1}\}^{0.5}}{2K_i^{-1}} \quad i=1,2 \quad (37)$$

The expressions obtained in the previous section can be used here also. The only difference is that for the probabilities P_{ij} ($i = 1, 2; 1 \leq j \leq 3$) Eqs. (35), (36), and (37) must be used.

Influence of Depropagation on n-Component Copolymerization

Let one of the monomers (M_1) be able to depolymerize. The initial suppositions and the scheme are the same as for ternary copolymerization in which only one monomer depolymerizes (the difference is in $n > 3$ monomers). In correspondence with the different possible ends of the growing chain, other positions of the system M_1, M_2, \dots, M_n are postulated here. A regular Markov chain with n positions is compared to the growth of the chain. The transition matrix of this chain is:

$$P = \begin{matrix} & & \begin{matrix} M_1 & M_2 & \dots & M_n \end{matrix} \\ \begin{matrix} M_1 \\ M_2 \\ \vdots \\ M_n \end{matrix} & \left| \begin{pmatrix} P_{11} & P_{12} & \dots & P_{1n} \\ P_{21} & P_{22} & \dots & P_{2n} \\ \dots & \dots & \dots & \dots \\ P_{n1} & P_{n2} & \dots & P_{nn} \end{pmatrix} \right. \end{matrix} \quad (38)$$

The transition probabilities P_{ij} ($2 \leq i \leq n$, $1 \leq j \leq n$) can be expressed by the formula:

$$P_{ij} = \frac{[M_j]r_{ij}^{-1}}{\sum_{j=1}^n [M_j]r_{ij}^{-1}} \quad (39)$$

The other n probabilities P_{ij} ($1 \leq j \leq n$) are expressed by the ratios:

$$P_{11} = \frac{[M_1] + \mu_1 K_1^{-1}}{[M_1] + \mu_1 K_1^{-1} + \sum_{k=2}^n [M_k]r_{ik}^{-1}} \quad (40)$$

$$P_{1j} = \frac{[M_j]r_{1j}^{-1}}{[M_1] + \mu_1 K_1^{-1} + \sum_{k=2}^n [M_k]r_{ik}^{-1}} \quad 2 \leq j \leq n \quad (41)$$

In this case $K_1 = k_{11}^{pol.}(k_{11}^{dep.})^{-1}$ is the equilibrium polymerization-depolymerization constant, while the parameter μ_1 is given by Eq. (42).

$$\mu_1 = \frac{[M_1] + \sum_{j=2}^n [M_j]r_{1j}^{-1} + K_1^{-1} - \{([M_1] + \sum_{j=2}^n [M_j]r_{1j}^{-1} + K_1^{-1})^2 - 4[M_1]K_1^{-1}\}^{0.5}}{2K_1^{-1}} \quad (42)$$

The limit vector $\alpha = (a_1, a_2, \dots, a_n)$ is again obtained as an eigenvector of the matrix P . To determine its components it is necessary for us to solve the linear system of equations (43).

$$\left. \begin{aligned}
 a_1(P_{11} - 1) + a_2P_{21} + \dots + \\
 a_1P_{12} + a_2(P_{22} - 1) + \dots + a_nP_{n2} = 0 \\
 \text{-----} \\
 a_1P_{1n} + a_2P_{2n} + \dots + a_n(P_{nn} - 1) = 0 \\
 a_1 + a_2 + \dots + a_n = 1
 \end{aligned} \right\} \quad (43)$$

Knowing the components a_i , we can find the necessary $n(n - 1)/2$ ratios of the monomer units concentrations in the copolymers. This gives a mathematical description of the copolymer composition based on the composition of the initial monomer mixture.

$$\frac{[m_i]}{[m_j]} = \frac{a_i}{a_j} \quad 1 \leq i, j \leq n \quad (44)$$

In this case, K_1 is also determined by an independent experiment, and the copolymerization constants r_{ij} can be determined by studying the binary copolymerizations of the possible monomer pairs.

The fundamental matrix of the studied regular chain is an n -dimensional matrix of the type (30). Analogously, on increasing the number of the components of the vector (32) to n , the vector of the limit dispersions in the examined case is obtained.

As in the case of ternary copolymerization where two monomers depolymerize, all cases when two, three, or n type monomer units are able to depropagate can be examined. Then a corresponding number of equilibrium constants $K_i = k_{ii}^{pol} \cdot (k_{ii}^{dep})^{-1}$ ($i = 1, 2, \dots, n$) and parameters μ_i ($i = 1, 2, \dots, n$) are introduced. For the determination of the parameters μ_i , expressions similar to Eq. (37) are used, where the upper limit of the sums is n . The transition probabilities P_{ij} are determined by expressions differing from Eqs. (19), (35), and (36) only in the upper limit of their sums. Further the equation for the composition of the copolymer is carried out in the same way as in the case when only one type of monomer units can depropagate. The difference in these two cases is in the expressions for the

transition probabilities P_{ij} and the parameters μ_i . The equation for the composition of the copolymers $[m_i]/[m_j] = a_i/a_j$ evidently can be used also when the copolymerization proceeds without depolymerization. At the determination of the components of the vector \bar{a} , however, it is necessary to eliminate the members including the equilibrium constants K_i and the parameters μ_i . It is obvious that after similar transformations Eq. (13) becomes the known Mayo-Lewis equation [13], while Eqs. (27) and (28) become those of Alfrey and Goldfinger [14]. The correctness of these equations is confirmed by the comparison between the experimental and calculated results for the composition of copolymers obtained in radical copolymerization of styrene (M_1), methyl methacrylate (M_2), acrylonitrile (M_3), and vinylidene chloride (M_4) at 60°C, as studied by Walling and Briggs [15]. The copolymerization constants are taken from Lewis, Mayo, and Hulse [16] and are:

$$r_{12} = 0.52 \pm 0.03$$

$$r_{13} = 0.41 \pm 0.08$$

$$r_{14} = 1.85 \pm 0.05$$

$$r_{21} = 0.46 \pm 0.03$$

$$r_{23} = 1.20 \pm 0.14$$

$$r_{24} = 2.53 \pm 0.01$$

$$r_{31} = 0.04 \pm 0.04$$

$$r_{32} = 0.15 \pm 0.07$$

$$r_{34} = 0.91 \pm 0.10$$

$$r_{41} = 0.085 \pm 0.01$$

$$r_{42} = 0.24 \pm 0.03$$

$$r_{43} = 0.37 \pm 0.10$$

The transitional probabilities calculated by Eq. (19) (the summation is made from 1 to 4) make up the transition matrix P of the regular Markov chain.

TABLE 2. Composition of the Tetrapolymer of Styrene (M_1), Methyl Methacrylate (M_2), Acrylonitrile (M_3), and Vinylidene Chloride (M_4) Obtained by Radical Copolymerization in Bulk at 60° C

No.	Monomer	Monomer in initial monomer mixture (mole %)	Monomer in copolymer (mole %)	
			Experimental ^a	Calculated
1	M_1	25.21	40.7	41.1
2	M_2	25.48	25.5	27.5
3	M_3	25.40	25.8	24.4
4	M_4	23.91	8.0	7.0

^aData of Lewis et al. [16].

$$P = \begin{matrix} & \begin{matrix} M_1 & M_2 & M_3 & M_4 \end{matrix} \\ \begin{matrix} M_1 \\ M_2 \\ M_3 \\ M_4 \end{matrix} & \left(\begin{matrix} 0.196 & 0.328 & 0.416 & 0.087 \\ 0.493 & 0.230 & 0.192 & 0.085 \\ 0.740 & 0.199 & 0.030 & 0.031 \\ 0.600 & 0.214 & 0.138 & 0.048 \end{matrix} \right) \end{matrix} \quad (46)$$

After solving the system (43) ($n = 4$) for the components of the limit vector, the following values are obtained: $\bar{\alpha} = (0.411; 0.275; 0.244; 0.070)$. By using Eq. (44) and the latter values ($n = 4$), the mole fractions of the different types of monomer units in the copolymer are obtained. They are compared with the experimental results in Table 2.

It is seen from Table 2 that the calculated and the experimental results correlate very well.

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